

NMR STUDIES
OF
ANTIMONY PENTACHLORIDE
DONOR-ACCEPTOR ADDUCTS
AND
HINDERED INTERNAL ROTATION
IN UREAS

PETER STILBS

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This review summarizes results from the following papers which will be denoted by reference numbers 1-6 :

1. Nuclear Magnetic Resonance Study of Hindered Internal Rotation in Urea in Solution.
P. Stilbs and S. Forsén
J. Phys. Chem., 75 (1971) 1901
2. The Barrier to Internal Rotation in Amides.
III. The Barrier to Internal Rotation, Dipole Moment and Conformation of 1,1-Dimethyl-3-isopropylurea.
P. Stilbs
Acta Chem. Scand., 25 (1971) 2635
3. Concerted Conformational Exchange Processes in Molecular Adducts of Antimony Pentachloride and N,N'-alkylureas.
G. Olofsson, P. Stilbs, T. Drakenberg and S. Forsén
Tetrahedron, 27 (1971) 4583
4. NMR Study of the Adducts of BF_3 and SbCl_5 with ^{15}N -labeled 1,3-Dimethylurea.
P. Stilbs
Tetrahedron Lett., (1972) 227
5. NMR Study of Donor Exchange Rates and Barriers to Internal Rotation in SbCl_5 Adducts of Some Carbonyl-Containing Compounds.
P. Stilbs
Tetrahedron, 29 (1973) 2269
6. A ^1H and ^{121}Sb NMR Study of Ionization Reactions in Antimony Pentachloride Donor-Acceptor Adduct Systems in Solution.
P. Stilbs and G. Olofsson
Acta Chem. Scand. Ser. (A), accepted for publication

Introduction.

Donor-acceptor adducts between metal halides with vacant orbitals and molecules containing electron pair donor groups, e.g. ketones, ethers, amides, amines and alcohols, are well known and have been studied by a large number of methods for a considerable period of time. The BF_3 -diethylether adduct is an example which probably is familiar to most chemists.

Several review articles and monographs on donor-acceptor adducts have appeared.⁷⁻¹³

The present work originated from the idea, originally proposed by Lappert,¹⁴ that electron-pair donor molecules containing a carbonyl group should have two preferred donor sites, corresponding to the two electron lone-pairs (Fig. 1).

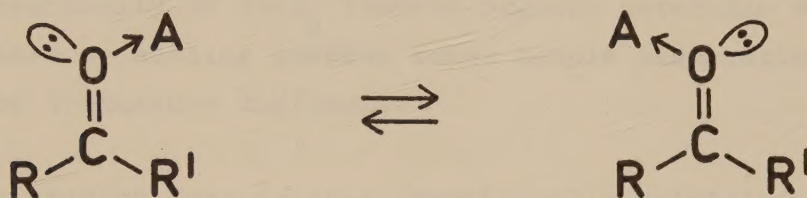


Fig. 1

At low temperatures, when exchange between these two conformers is slowed down, a doubling of the PMR signals from the R-groups would be expected. Apart from intuitive arguments for this expectation, protonated carbonyl compounds of analogous structure had been detected by PMR¹⁵ and an X-ray crystal structure determination of $\text{SbCl}_5 \cdot \text{HCON}(\text{CH}_3)_2$ ¹⁶ indicated that in this adduct the $\text{C}=\text{O} \rightarrow \text{A}$ angle (124.5°) differs significantly from 180° in the solid state.*)

*) The following abbreviations will be used: A=acceptor, D=donor, DMU=1,3-dimethylurea, DMF=N,N-dimethylformamide, DMA=N,N-dimethylacetamide, DMSO=dimethylsulphoxide, TMU=1,1,3,3-tetramethylurea, TrMU=1,1,3-trimethylurea, HMPT=hexamethylphosphorous triamide, EtOAc=ethyl acetate, X=halogen.

An investigation was undertaken, and SbCl_5 was chosen as acceptor for the following reasons: i) these or similar adduct systems had previously been studied by Olofsson¹⁷ by calorimetric methods and the thermodynamic parameters for adduct formation were known, providing valuable reference information; ii) the adducts are often very soluble, facilitating low-temperature studies; iii) SbCl_5 gives predominantly 1:1 adducts^{7,8,17} and may be characterized as a strong acceptor^{7,8,17}; iv) inert low- and high-temperature solvents suitable for PMR measurements such as CH_2Cl_2 , CHCl_3 and $\text{CHCl}_2\text{CHCl}_2$ and deuterated analogs are readily available; v) SbCl_5 is relatively simple to handle since it is a liquid at room temperature (mp. 3°)¹⁸ and it is commercially available in high purity.

Some disadvantages are also experienced with this acceptor: i) usually NMR spectra cannot be observed from the acceptor part of the adduct; ii) the low vapour pressure ($6 \text{ mm}/48^\circ$)¹⁸ and the high reactivity of SbCl_5 towards organic materials such as vacuum grease or sealing gaskets makes sample preparation by vacuum line techniques difficult.

The donors studied were various symmetrically substituted molecules, such as acetone, diethylketone, dimethylcarbonate and tetramethylurea. The expected doubling of adduct PMR signals was not found in the systems studied at that time even at temperatures close to the freezing point of CH_2Cl_2 ($\approx -95^\circ$). Some unpublished observations of a later date will be discussed below. Henriksson and Forsén later found the expected effect in the BF_3 -diethylketone adduct below -110° .¹⁹

One of the last studied molecules in the above-mentioned series was 1,3-dimethylurea (DMU). Two methyl PMR signals were already present below 30° in the spectrum of the SbCl_5 adduct of this compound. This was tentatively interpreted as being due to restricted rotation around the N-C bonds. Further studies of this and related systems led to papers 3-5 where this interpretation was found to be mainly correct.

In analogy with the findings of Gore et al. on the DMF-BF_3 adduct,²⁰ it was observed that adduct formation increases the barrier to internal rotation about the amide bonds. As a natural consequence of this it was reasoned that it should also be possible to observe hindered internal rotation in uncomplexed ureas at low temperatures. In contrast to the very large number of studies on simple amides,²¹ no such observation on urea or simple alkylureas had been published at the time. Studies on this subject were undertaken, and subsequently led to papers 1 and 2.

At an early stage of the work connected with paper 3, some inconsistencies in the PMR shifts in the adduct systems were noted, indicating that the chemical equilibria in these systems were not as simple as initially assumed. Further investigations of these effects led to paper 6, where partial ionization of donor-acceptor adducts is studied by PMR and by ^{121}Sb NMR, and to the work by Olofsson and coworkers on the ternary $\text{H}_2\text{O}\cdot\text{D}\cdot\text{SbCl}_5$ ²² and $\text{HCl}\cdot\text{D}\cdot\text{SbCl}_5$ adduct systems.^{22,23}

Independent studies on systems analogous to those in papers 3 and 6 have been made by Hartman and Schrobilgen.^{24,25} To a large extent these two investigations confirm each other.

Asymmetric bonding at the donor site in adducts in solution.

As mentioned in the introduction, the initial subject of this investigation was exchange phenomena similar to that illustrated in fig. 1. A number of unpublished investigations related to the findings of Henriksson and Forsén have been made and some will be briefly quoted here.

Two similar types of exchange processes are possible in this case, as illustrated in fig. 2. (For spectroscopic measurements on the conformations of dialkylketones, see e.g. ref. 26).

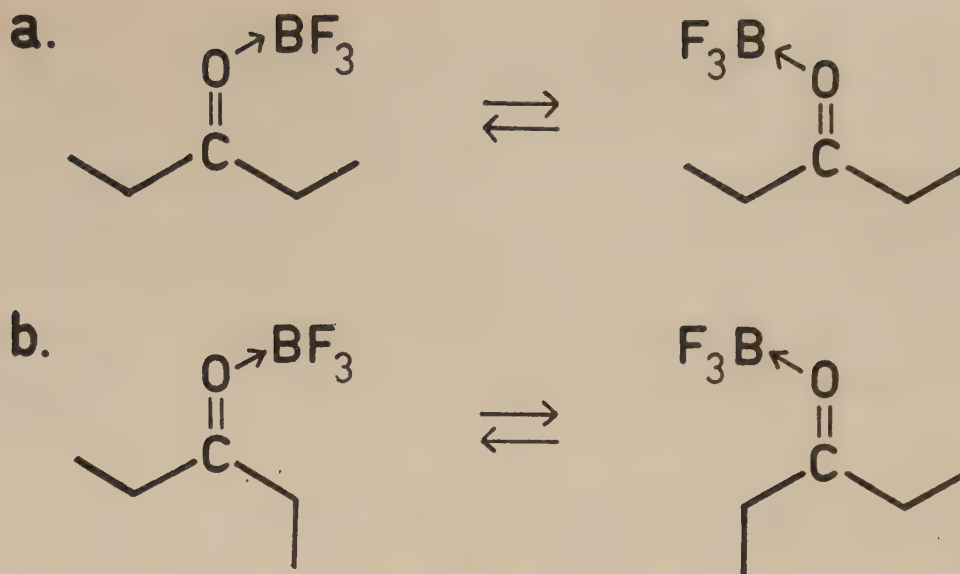
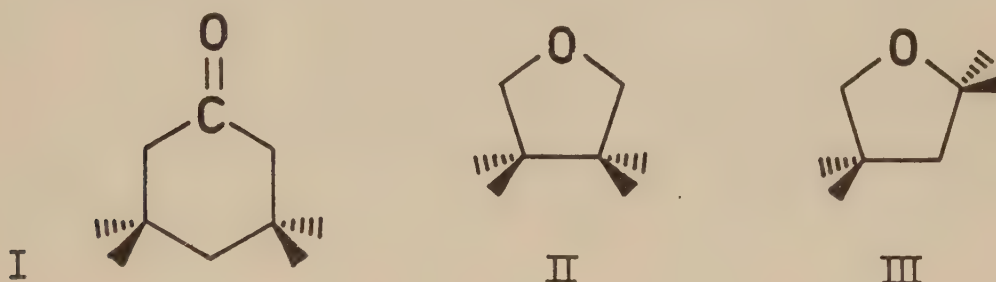


Fig. 2

The "2b" type of exchange seems most likely from steric considerations, but it is doubtful that alkyl group rotation affects the exchange rate. In order to investigate this, the BF_3 adduct of 3,3,5,5-tetramethylcyclohexanone (I) was prepared and studied.²⁷



In this cyclic adduct the alkyl groups are locked, and still a slow exchange of the type in fig. 1 was found, indicating that alkyl group rotation in open chain analogues does not retard the exchange. The NMR lineshape changes even take place at a temperature $\approx 30^\circ$ higher than that in the diethylketone adduct.²⁸

The same adduct system has also been studied by Torri and coworkers,²⁹ with very similar results but a different interpretation, *viz.* a decreased chair-chair inversion rate upon adduct formation (Fig. 3).

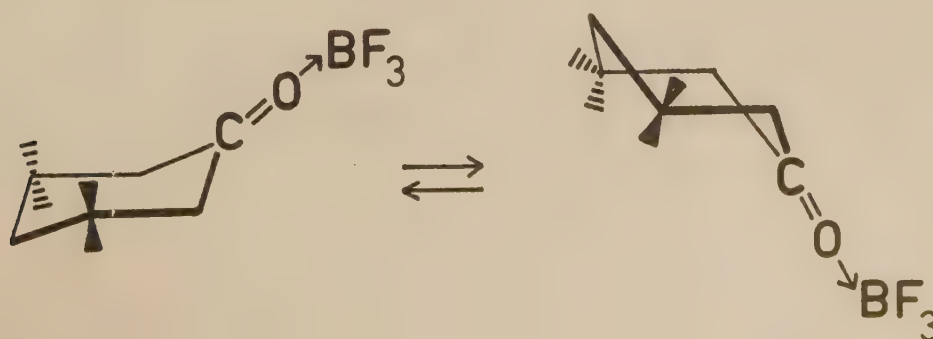


Fig. 3

These workers do not consider interpretations like the one given by Henriksson and Forsén and give no reference to this work. Their interpretation is doubtful since in a fixed chair form the 2-methylene protons become magnetically non-equivalent, and a significant geminal spin-spin coupling of the order of 10-15 Hz^{*)} should be observed in the PMR spectra. (Cf. the work of St.-Jacques *et al.* on inversions in related ring systems³⁰.) The geminal methyl groups and the 4-methylene protons should also become non-equivalent at low temperatures, contrary to observations.

Ether analogues of these adducts have some interest in connection with these problems. The BF_3 adducts of the compounds II and III^{27,31} have been studied at low temperatures.²⁸ At 60 MHz the CH_2 and CH_3 PMR signals from the adducts are very broad (≈ 15 Hz) at the lowest attainable temperature of the spectrometer ($\approx -135^\circ$), but since no asymmetric forms could be frozen out the results could not be made conclusive. It is however clear that if asymmetric bonding occurs at the ether oxygen atom, exchange between the conformers is faster than in ketones.

As discussed in papers 3-5, 1,3-dialkylurea adducts represent a special case of asymmetric bonding. Here it was found very likely that the two forms illustrated in fig. 4 represent the conformers of lowest energy.



Fig. 4

*) Geminal spin-spin couplings in this system are not known, and might be small, but an exploratory study of the SbCl_5 ·epicamphor adduct at -20° suggests a value of 12 Hz, which is slightly larger than in uncomplexed epicamphor. Epicamphor has an unstrained 6-ring system similar to I.

In this type of adduct restricted rotation around the amide bonds is rate-determining, and the steric interactions between the acceptor and the alkyl groups determines the populations of the two forms,³⁻⁵ which become very similar in many cases even if $R \neq R'$, as discussed in paper 3. Similar results were obtained by Hartman and Schrobilgen on analogous BF_3 adduct systems.²⁴

Competitive coordination in urea adducts.

Oxygen and nitrogen coordination are both possible alternatives in SbCl_5 and BF_3 adducts of alkylureas. Greenwood and Robinson³² originally suggested that nitrogen coordination was favoured in N,N'-alkylureas although the opposite would be expected from Pearsons hard-soft acid-base (HSAB) classification theory,³³ as pointed out by Garnovskii *et al.*³⁴ There is now convincing evidence for oxygen coordination for SbCl_5 adducts (papers 3-5), as well as for BF_3 adducts (Refs. 24,35 and paper 4). One additional experiment was performed on the adduct type in order to cast further light on the question of whether oxygen or nitrogen coordination takes place. The SbCl_5 adduct of 1-methyl-3-benzyl-urea was prepared and studied in CDCl_3 solution.³⁶ If this adduct does not have a plane of symmetry, the methylene protons of the benzyl part should appear as AB quartets in PMR³⁷ under conditions where the intramolecular exchange process under consideration is slow (Fig. 5).

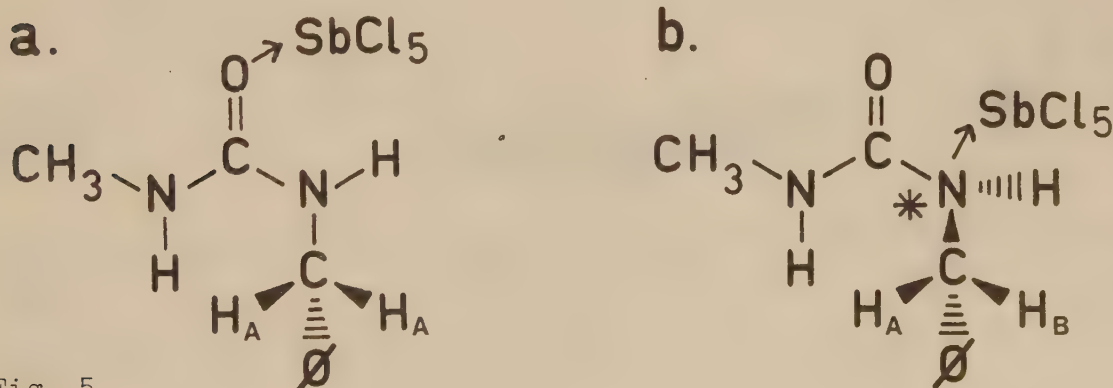


Fig. 5

The methyl and methylene parts of the low-temperature spectrum from this adduct are illustrated in fig. 6.

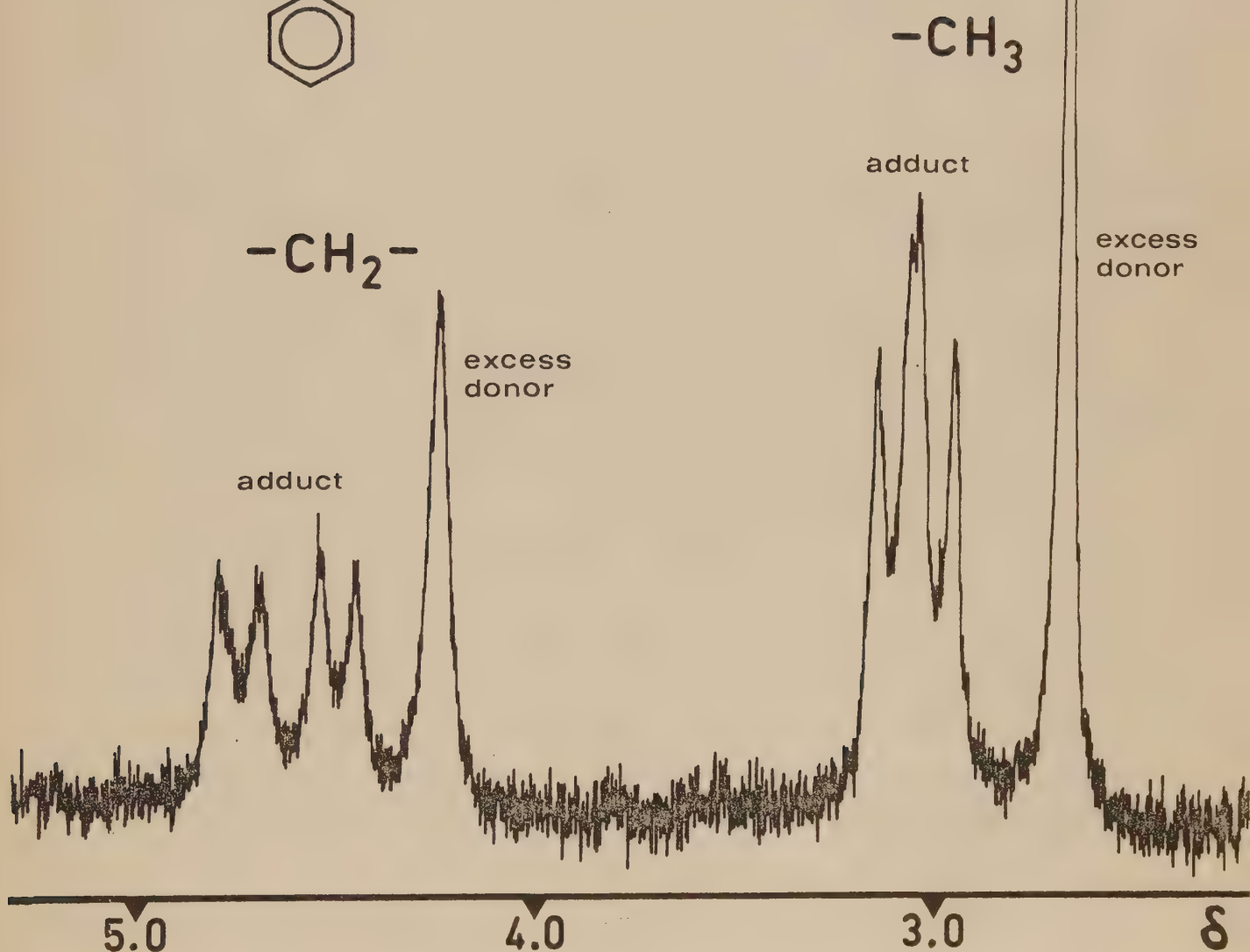
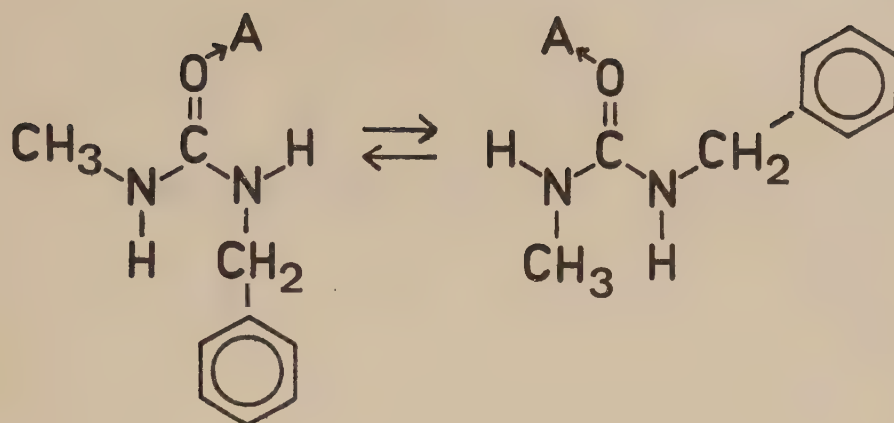
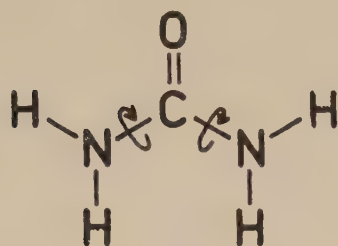
^1H 60 MHz

Fig. 6 PMR spectrum of the 1-methyl-3-benzylurea adduct at -20° .

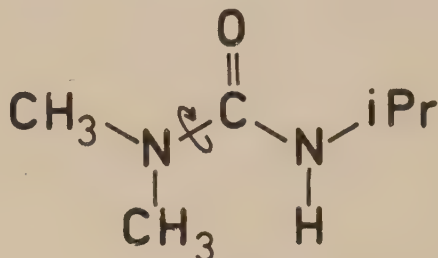
Intermolecular donor exchange is slow, the $-\text{CH}_2-$ signals do not appear as AB quartets, there is no intramolecular averaging exchange process consistent with the spectrum, and thus the adduct must have a plane of symmetry. This provides additional proof that O-coordination and not N-coordination is taking place (fig. 5).

Studies of hindered internal rotation.

a. Free ureas. Since the measurements of amide barriers to internal rotation in urea (IV)¹ and in 1,1-dimethyl-3-isopropylurea (V)²,



IV



V

a number of other similar measurements have appeared in the literature, and observations can now be compared and generalized (Table 1).

Although many of these $\Delta G^\ddagger$ values have low precision since they were obtained under difficult conditions of measurement and with the use of several approximations in the calculations, the following can be noted: i) with reference to the unsubstituted compound mono-alkylsubstitution increases the amide barrier in this bond; ii) further substitution at the other nitrogen decreases the barrier towards the value for the parent compound; iii) obviously at least three rotamers are present in the 1,3-dialkylsubstituted compounds. Therefore it seems likely that upon alkyl substitution the barrier changes are primarily due to conjugative effects and that the steric interactions between a 1-alkyl group and a 3-NH proton are small. A trend towards a barrier increase in the series oxo-thio-seleno is apparent, in line with observations on simple amide systems.^{38,39}

Table 1. Barriers to internal rotation in ureas and alkylureas.

Compound	$\Delta G^\ddagger$ /kcal.mol ⁻¹	Temp/K	Solvent	Ref.
urea (A)	11.2	222	DMF	1
	11.0	225	DMF/acetone	42
thiourea (A)	12.8	259	DMF/acetone	42
	11.3	227	methanol	40
selenourea (A)	12.8	257	DMF/acetone	42
	12.4	239	methanol	40
methylurea (B)	7.5 ^c	150	methanol	41
methylthiourea (B)	15.1	285	methanol	41
(A)	10.2	203	methanol	41
(B)	14.4	302	D ₂ O	43
1,3-dimethylurea (B)	7.5	150	methanol	41
1,3-dimethylthiourea ^a (B)	11.8	232	methanol	41
1,3-diethylthiourea ^{a,b} (B)	11.2	230	acetone	44
1,1-dimethylselenourea (C)	14.6	298	CDCl ₃	38
1,1-dimethyl- 3-isopropylurea (C)	9.7	298	CHFC1 ₂ /C ₇ H ₇ F	2
1,1,3-trimethylthiourea(C)	10.6 ^d	211	CDCl ₃	45

(A)= C-NH₂ barrier , (B)= C-NHR barrier, (C)= C-NR₂ barrier

a. At least three (two equivalent) conformers are present in these measurements, although the calculations have been made with two-site lineshape equations.

b. Estimated from given spectra.

c. This value seems too low. I have been unable to reproduce any lineshape changes due to restricted rotation under similar conditions, and this value is consequently neglected in the discussion.

d. Gattegno et al.⁴⁶ have confirmed this value and also present a CNDO/2 calculation, which supports the conformational assignments in refs. 2 and 45.

b. Amide torsional barrier changes upon adduct formation.

The coordination of an electron pair acceptor at the oxygen atom in an amide increases the double bond character of the C-N bond and nitrogen coordination decreases it. This is schematically illustrated in fig. 7.

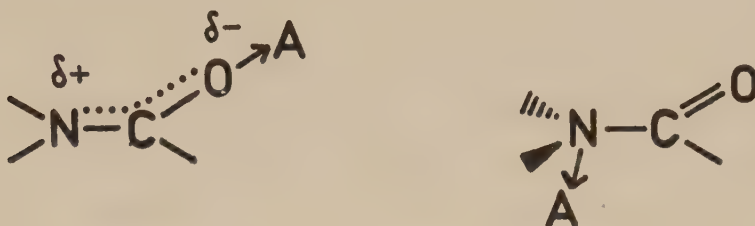


Fig. 7

In paper 5 a study of a number of amide-type SbCl_5 adducts is presented. The barriers to internal rotation are invariably increased as compared to the parent compounds ($3\text{--}5 \text{ kcal mol}^{-1}$). These studies have later been extended to other metal halides and reference donor amides, although considerable experimental difficulties have hampered the progress of this study. It is however evident so far that GeCl_4 and N,N -dimethyltrichloroacetamide do not seem to interact, as judged from PMR spectra. In 1,1,2,2-tetrachloroethane solution no shift ($< 0.002 \text{ ppm}$) of the methyl signals is observed upon addition of nearly equimolar amounts of GeCl_4 , and the coalescence temperature of the dimethylamino doublet is unchanged (within $\pm 0.5^\circ$).²⁸ This casts doubt on the work of Matsubayashi and Tanaka,⁴⁷ where a considerable barrier decrease was found in SiCl_4 and GeCl_4 -benzamide- CH_2Cl_2 mixtures as compared to the free benzamides in CH_2Cl_2 . Acidic impurities in the samples could explain their observations, since this may affect amide barriers through partial coordination of the acid to the nitrogen atom. A calorimetric and PMR study of the DMA- $\text{HCl-CH}_2\text{Cl}_2$ system has been made by Bernander and Olofsson.⁴⁸

c. Uncertainties in the measurements of barriers to internal rotation.

Most sources of error in the underlying experiments and calculations have already been discussed in papers 1-3 and 5, or reference is given to such discussions, but there is one type of approximation which has invariably been used in all published studies on amide barriers in dimethylsubstituted amides. Strictly speaking, the

application of the lineshape equation for an uncoupled two-site case (see Appendix) to this type of spin system is an approximation, but nonetheless a rather good one. There is a small spin-spin coupling between these methyl groups as well as a spin-spin coupling between the methyl groups and the nitrogen atom. Usually these are unresolved and appear only as a broadening of the dimethylamino signal(s), accounted for by the T_2 terms in lineshape simulations. The unresolved splittings in the PMR spectra due to the proton-proton coupling disappear at high temperatures where the methyl groups become magnetically equivalent. The case is reversed with regard to the proton-nitrogen coupling, the effects of which disappear at low temperatures as a result of a faster ^{14}N relaxation rate due to the increase in the solvent viscosity. Therefore these two line-broadening effects tend to balance each other.

Since most of the studies in papers 1-3 and 5 concern ureas, estimates of these and other neglected couplings in this type of spin system are of interest for the discussion. The PMR spectra of two doubly ^{15}N labeled model compounds, urea and 1,3-dimethylurea have been analyzed^{49a,50} at 40° , where the rotation around the amide bonds is fast on the PMR time scale. The results, with reference to fig. 8, are summarized in table 2.

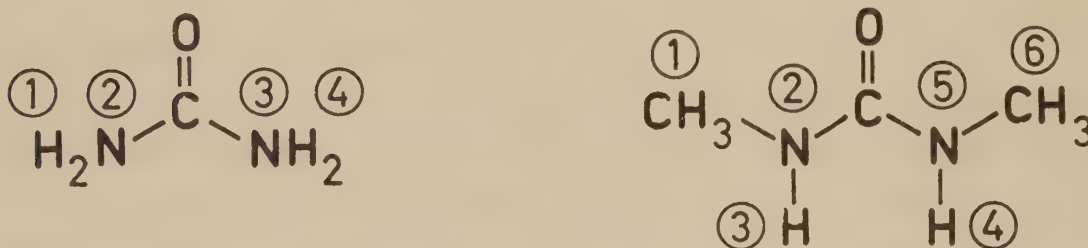


Fig. 8

Table 2. Observed spin-spin couplings in Hz (in 99.9% deuterated DMSO).

a. $^{15}\text{N}_2$ -urea				b. $^{15}\text{N}_2$ -1,3-dimethylurea					
	②	③	④		②	③	④	⑤	⑥
①	86.6	1.9	1.0	①	.7	4.7	.05	*	*
②		5.1	1.9	②		88.7	.1	5.3	*
③			86.6	③			*	.1	.05
				④				88.7	4.7
				⑤					.7

(* less than .05 Hz)

There is some coupling constant sign information in these PMR spectra,

but in the DMU case the effects are small and the results are uncertain without additional spin decoupling experiments. For urea it is apparent that the one- and three-bond proton-nitrogen couplings have the same sign. It has not been possible to evaluate the two-bond proton-proton coupling in urea at low temperatures, nor in partly deuterated samples, due to broadening effects. It is certainly less than 5 Hz.

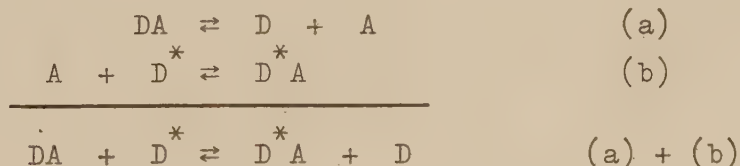
The four-bond methyl-methyl proton coupling in neat TMU at 40° has been evaluated from the ^{13}C satellite PMR signals to be less than 0.15 Hz.

Experimental spectra invariably indicate that the effects from the nitrogen-methyl coupling have already disappeared at 40° in unlabeled compounds in the solvents used in this work.

The errors due to the neglect of residual spin-spin couplings therefore seem reassuringly small. One exception may be the urea system, but for estimates of $\Delta G^\ddagger$ for the restricted rotation near the coalescence temperature (see Appendix) the errors are small. This aspect has been further discussed by Walther *et al.*⁴²

Donor exchange reactions.

In paper 5 a quantitative study of the relation between ΔH values for adduct formation and $\Delta H^\ddagger$ values for the donor exchange process for some SbCl_5 adducts was made. Soon after the submission of this article a similar study on the $\text{BX}_3\text{-CH}_3\text{CN}$ adducts appeared.⁵¹ Both these studies led to the conclusion that the rate-determining step in donor exchange is dissociation of the adduct (a),



and that there is a close correspondance between these ΔH and $\Delta H^\ddagger$ values. Comparison between previously measured thermodynamic SbCl_5 adduct formation parameters ΔH and ΔS ¹⁷ and the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values in paper 5 suggests the following very schematic energy profiles for adduct formation (Fig. 9) :

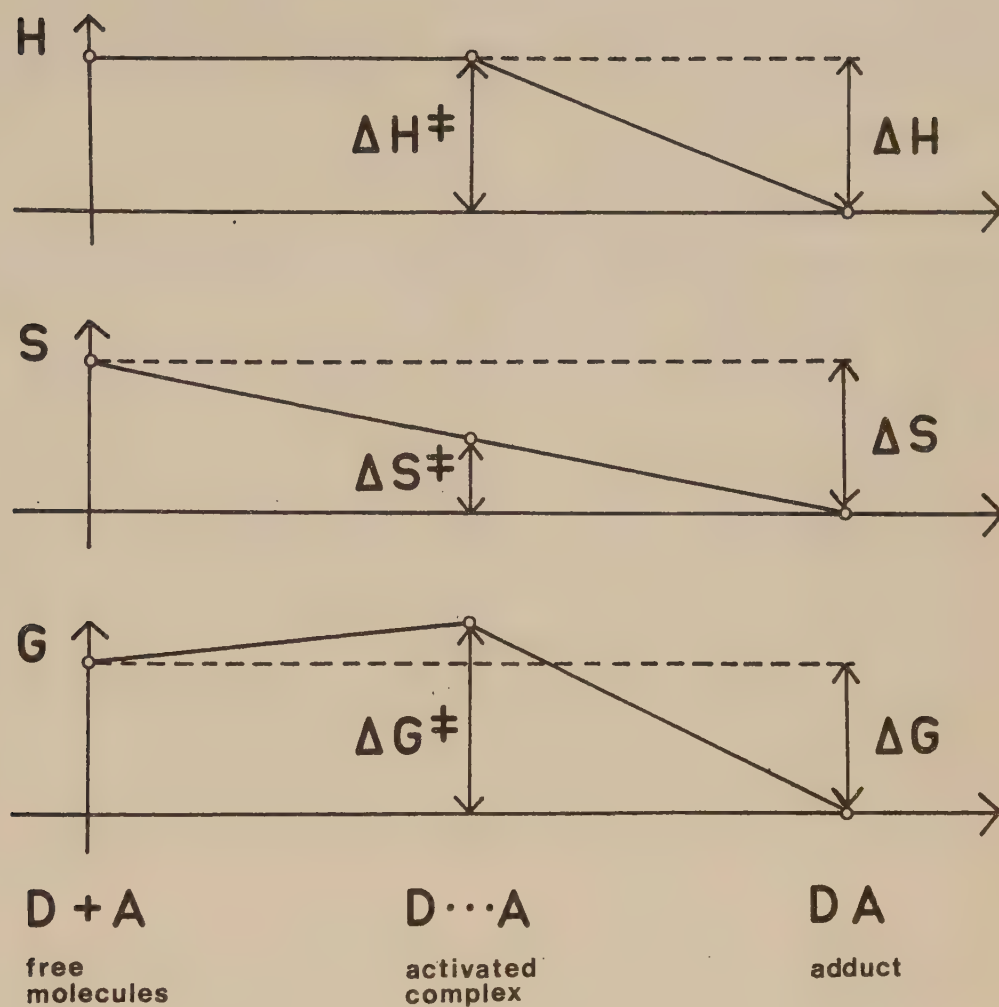
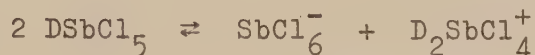


Fig. 9 Schematic energy and entropy profiles for SbCl_5 adduct formation (arbitrary vertical scales).

Ionization reactions in SbCl_5 adducts.

In paper 6, measurements of partial autoionization of SbCl_5 adducts of the strong donors DMSO, TMU and HMPT, as well as similar preliminary results on DMU and DMF adducts, are presented. It was found by ^1H and ^{121}Sb NMR that, in contrast to the weaker EtOAc adduct, a significant fraction of these adducts is autoionized in solution:



The systems are complicated, and strong indications of rapid exchange processes between different species were also found. The donor molecules in the $\text{D}_2\text{SbCl}_4^+$ ion probably are in rapid exchange with the donor in DSbCl_5 when the D/SbCl_5 ratio is less than 1.0, and with excess donor above this ratio. Necessarily then the averaged ^1H NMR signal from the "adduct" donor must sharply change from the average of the adduct+ $\text{D}_2\text{SbCl}_4^+$ signals to the "pure" adduct signal at the D/SbCl_5 ratio 1.0, since above this ratio donor in $\text{D}_2\text{SbCl}_4^+$ is instead in rapid exchange with excess donor. It was however found that the ^1H NMR shift of the TMU adduct signal does not change significantly at the 1.0 ratio but, as discussed in paper 6, there are indications that the ^1H NMR shifts of donor in $\text{D}_2\text{SbCl}_4^+$ and the unionized adduct are closely the same, making the resultant shift change small.

Reexamination of spectra recorded in connection with paper 3 show a small but clear change in appearance at the 1.0 ratio of the low-temperature "adduct signal" from the DMU and TrMU adducts.

A much more sensitive parameter should be the average barrier to internal rotation around the amide bonds in these adducts. In paper 3 no explanation could be given for the 10-15° and more than 50° changes in coalescence temperatures between samples with excess DMU or TMU and excess SbCl_5 . A very attractive explanation is exchange averaging of the $\text{D}_2\text{SbCl}_4^+$ and DSbCl_5 barriers. The value of the former barrier is not known, but it seems unreasonable that it could be higher than the DSbCl_5 barrier.

^{13}C NMR and laser Raman spectroscopy should be useful for further studies on these ionization reactions.

The question arises if the partial ionization has any connection with the measured barriers to internal rotation in the adducts and the rates of donor exchange in paper 5. The answer should be no, since the barriers measured were obtained from a "pure adduct" signal and the donor exchange rates were based on the mean lifetime of the adduct.

Appendix.

Kinetic NMR measurements.

Reversible molecular exchange processes with rates in the approximate range 0.0001 - 0.1 seconds can often be studied by means of high resolution NMR spectroscopy. Many types of exchange can be brought into this rate region by a suitable temperature change.

In the present work restricted rotations around amide bonds (papers 1-3,5) and/or donor exchanges in donor-acceptor systems (paper 5) have been investigated with this method. These two types of exchange are illustrated in fig. 10.

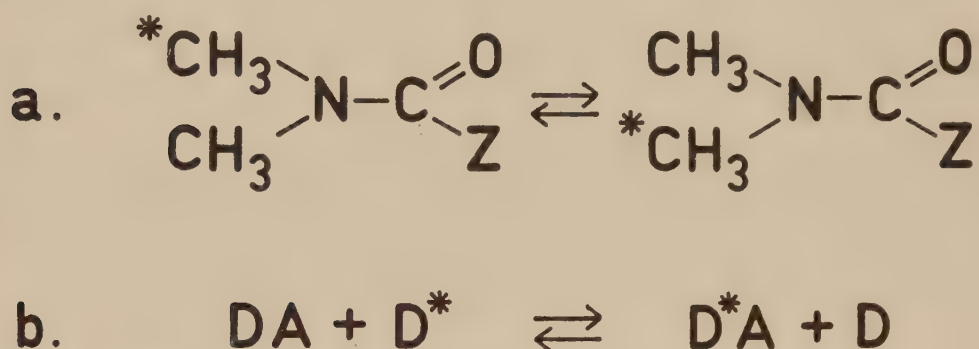


Fig. 10

If we for example consider the restricted rotation process in fig. 10, two PMR signals corresponding to the two methyl groups will in general be observed if rotation is slow around the amide bond, and one signal if it is fast. At intermediate exchange rates broadened signals will be observed. A few examples of typical lineshapes are illustrated in fig. 11. The lineshape in fig. 11c is called the coalescence lineshape. Here the mean lifetime of individual rotamers is given by $\sqrt{2}/(\pi \delta\nu)$, with $\delta\nu$ expressed in frequency units. This provides a reference point for the classifications "fast" and "slow" on the NMR time scale.

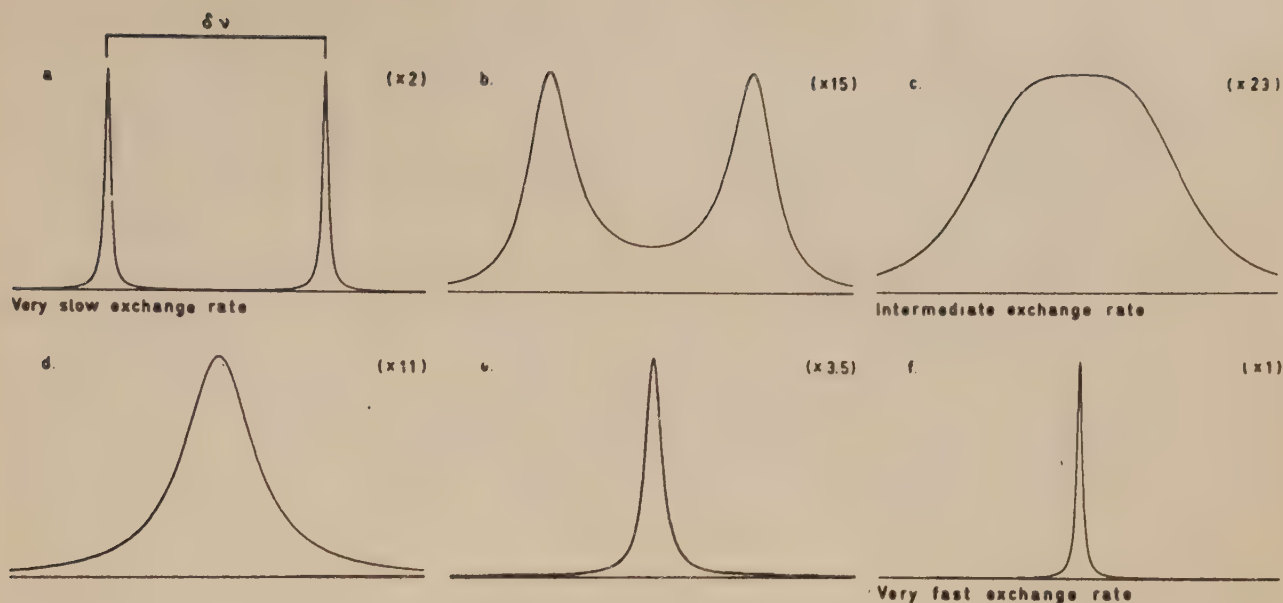


Fig. 11 Simulated PMR spectra for a "two-site" exchange process, as in fig. 10a. The amplitude factor has been adjusted with the amounts indicated to give a constant height of the signals.

The NMR lineshape is thus related to the exchange rate. From a set of lineshape measurements at known temperatures, estimates of activation parameters for the exchange process can be evaluated from the resulting rate constants.

The mathematical background for NMR lineshape measurements will not be reproduced here. The basic theory was originally developed by Gutowsky et al.⁵² and has later been further extended by several workers in the NMR field. A relatively extensive up-to-date review of the subject with many application examples has been given by Sutherland.⁵³ It is found that even in the simplest case, the so-called uncoupled, equally populated two-site case illustrated above, the lineshape expression becomes relatively complicated and calculations are preferably done with the aid of a computer, or at least with a programmable calculator with a plotter.

Apart from magnetic field inhomogeneity, scale factors and positioning parameters, the lineshape is under normal measuring conditions a function of the exchange rate or mean lifetime of the species (τ),

the "nonexchanging" shift difference between the two signals ($\delta\nu$ in fig. 11) and the transverse relaxation times (T_2) of the nuclei in the two sites. In principle all these parameters are temperature dependent and one major problem with the measurements is that these parameters cannot be independently evaluated in the intermediate exchange rate range. A form of interpolation between T_2 values extracted from the very slow and very fast exchange spectra and extrapolation of slow exchange $\delta\nu$ values is therefore employed. At fixed estimates of $\delta\nu$ and T_2 the desired exchange rate can be extracted from the observed spectra by matching them to the line-shape function. This can either be done visually with computer-plotted spectra or numerically. Both these methods have been used in the present work.

The numerical fitting was done by a computer treatment of digitized spectra in the form of paper tape which could be automatically punched via an analog/digital converter and a paper tape punch interfaced to the spectrometer recorder output and X-axis step motor drive. This tape contains 50-200 equidistant points of the observed spectrum in the form of 4-digit numbers. The value of a particular number is related to the absorption intensity at the corresponding point in the spectrum. The best fit in the least-squares sense is obtained by adjusting lineshape parameters in the theoretical function to minimize the sum over all data points of $(F_i^{\text{obs}} - F_i^{\text{calc}})^2$, where F_i is the normalized and scaled absorption intensity at the point i . The minimization adjustment was accomplished with the FORTRAN subroutine STEPIT.^{49b} These measurements and calculations are further discussed in papers 2,3 and 5.

Two non-standard measurements have been made. In paper 2 a line-shape measurement was made at two frequencies in order to improve the estimates of $\delta\nu$ and T_2 , and in paper 5 an automatized method was used for the estimation of errors in τ -values and activation parameters arising from uncertainties in $\delta\nu$ and T_2 .

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